(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 045 500**
B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 23.10.85

(21) Application number: 81106038.3

(22) Date of filing: 31.07.81

(51) Int. Cl.⁴: D 21 C 3/02, C 12 N 1/22, C 12 P 21/00, C 13 K 1/02

(54) Method for pretreatment of cellulose materials.

(30) Priority: 31.07.80 JP 104285/80

(43) Date of publication of application:
10.02.82 Bulletin 82/06

(45) Publication of the grant of the patent:
23.10.85 Bulletin 85/43

(84) Designated Contracting States:
DE GB SE

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The file contains technical information submitted after the application was filed and not included in this specification

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Description

The present invention relates to a method for the pretreatment of lignocellulose materials for improving the process of biologically or enzymatically decomposing lignocellulose materials.

When microorganism proteins are prepared by reacting a cellulose material such as rice straw, wheat straw, bagasse, waste paper or wood dust with a cellulose decomposing fungus or bacterium and propagating a cellulase or organic acid secreted by the cellulose decomposing fungus or bacterium, or when an alcohol and an organic acid are prepared by reacting a cellulose material with a cellulase to convert cellulose to glucose and then reacting the treated cellulose material with an enzyme or bacterium, it is necessary to apply a pretreatment step for destroying the structure, since the cellulose material has a structure which hardly is attacked by the action of a cellulase.

Cellulose of a lignocellulose material is composed of a homopolymer comprising glucose units linearly arranged through β-1,4-linkages, and cellulose has a crystalline structure in which these linear homopolymers are arranged in parallel to one another and it is covered with hardly decomposable lignin. The cellulase secreted by the cellulose decomposing fungus or bacterium is a composite enzyme comprising C_1 enzyme rendering crystalline cellulose amorphous, Cx enzyme decomposing amorphous cellulose into cellobiose and β-glucosidase decomposing cellobiose to glucose. However, since this composite enzyme has no function of decomposing lignin, the enzyme can hardly react directly with cellulose. Furthermore, cellulases secreted from cellulose decomposing fungi or bacteria isolated up to the present are weak in the activity for rendering crystalline cellulose amorphous, that is, the C_1 activity. Accordingly, since cellulose in a cellulosic material is hardly decomposed by presently available cellulases, in order to increase the efficiency of converting the cellulose material to valuable substances such as glucose and microorganism proteins by the biological decomposition of the cellulose material, a pretreatment should be carried out for decomposing lignin and for decreasing the crystallinity of cellulose.

There are three categories of pretreatments known in the art: (See "Physical and Chemical Pretreatments for Enhancing Cellulose Saccharification" by Merril et al, pp. 125—153 (1976), and "production of Microorganic Protein from Residues and Wastes" by T. Ishihara, Lumber Industry, vol. 34—5 (1979)).

1) Chemical Pretreatment where various chemical substances are used. Among the chemical substances are examplfied ozone, sodium chlorite-acetic acid, boiling caustic soda solution, boiling hydrochloric acid solution, aqueous ammonia solution, aqueous sulfuric acid solution, ethylamine, and phosphoric acid solution.

Ozone and sodium chlorite are used in combination as an oxidizing agent for lignin to lignocellulosic material. Sulfuric acid, hydrochloric acid and phosphoric acid are used to lower the crystallinity of cellulose. These chemical agents do not satisfactorily increase the degree of enzymatic saccharification of cellulose.

2) Physical Pretreatment including finely grinding with ball-mill, irradiation with γ-rays and irradiation with ultra-violet rays. These physical pretreatment methods have almost no practical value because they need a large amount of energy.

3) Microbiological Pretreatment with bacteria for destroying cellulose or hemicellulose or with bacteria for decomposing lignin. These microbiological processes generally require a long period of time because of their slow microbial reaction rate.

After an extensive study of the pretreatments, it has been revealed that chemical pretreatments have advantages over other pretreatments.

In one of the known ozone pretreatments powdered cellulose is dispersed and suspended in water and an ozone-containing gas is supplied into the suspension, whereby ozone reacts with lignin and decomposes it. As the O_3-lignin reaction takes place, lignin is decomposed to produce low molecular weight compounds, which react with ozone and consume ozone. Accordingly, the above-mentioned ozone treatment needs a very large amount of ozone.

In the other process of ozone pretreatment, an ozone-containing gas is contacted with powdered dry or wet cellulose to chemically decompose lignin therein. This process needs a large amount of ozone because the reactivity between lignin in dry or wet cellulose and ozone is not high.

On the other hand, a known alkaline pretreatment uses an aqueous caustic soda solution in which powdered cellulose is dispersed and suspended in the caustic soda solution and the suspension is heated to extract lignin from the cellulose. In this process, about 200 g of NaOH per 1 kg of rice straw is needed, which is also too expensive for the commercial use. When the ozone pretreatment is applied to the other chemical pretreatments such as processes using methanol-hydrochloric acid, aqueous ammonia or ethylamine, ozone is consumed in large amounts because CH_3OH, NH_4OH and ethylamine react with ozone, rather than with lignin.

Soluble lignin contained in waste water discharged from the step of pulping wood in the paper-making industry is decomposed by ozone (see the research of Takamasa Higuchi, sponsored by the Ministry of Education in 1975 with the title "Decomposition of Lignin in Waste Water by Treatments with Ozone and Microorganisms; Research Report of Purification of Environment). Ultraviolet ray decomposition of cellulose is performed at a higher efficiency in an air atmosphere than in a nitrogen atmosphere (see

General Organic Chemistry, Natural Polymeric Compounds, Volume I, page 42, published by Asakura Shoten).

In Nutrition Reports International, August 1979, Vol. 20, No. 2, p. 179—182 studies on the effect of sodium hydroxide and ozone treatments of cotton straw are described, which have been carried out in order to make cotton straw available as a ruminant fodder. According to this article the ground cotton straw is first treated with a concentrated solution of sodium hydroxide and then kept under anaerobic conditions for an extended period. After this treatment the steps of ozonation is carried out.

During the prolonged storage of the straw treated with NaOH lignin of the material is further decomposed and dissolved in the sodium hydroxide solution, with the result that in the following step of ozone treatment ozone reacts preferentially with the dissolved lignin rather than with undissolved lignin in the material. Therefore ozone is consumed by the undesirable reaction with the dissolved lignin and the process for treating the undissolved lignocellulose material becomes ineffective and less economical.

In view of the described prior art studies were carried out in order to develop a method for the pretreatment of lignocellulose materials by using the decomposition by an ozone treatment, which may be carried out with high effectiveness and in an economical manner without excessive side reactions and without an unduly high composition of ozone.

It has been found that when a lignocellulosic material, which is impregnated with an alkaline aqueous solution of an alkali metal or alkaline earth metal compound, especially sodium hydroxide, is contacted and reacted with ozone in the state of gas-solid contact, the biological decomposability of the cellulosic material can be remarkably improved.

According to the present invention there is provided a method for the pretreatment of lignocellulose materials for biologically or enzymatically decomposing cellulose materials, in which a cellulose material is treated with an alkaline aqueous solution of an alkali metal or alkaline earth metal compound and afterwards with ozone, which is characterized in that after the treatment with the alkaline solution the cellulose material is immediately treated with ozone in the state of gas-solid contact.

According to the present invention, the utilizability of a lignocellulose material by a cellulolytic fungus or bacterium and the enzymatic decomposability of cellulose by the cellulase can be improved by the above-mentioned pretreatment.

As cellulose materials, there are examplified rice straw, wheat straw, bagasse, waste paper and wood dust. These cellulose materials are used after they have been chopped into 0.5 to 10 mm, preferably 5 to 10 mm in length, for example.

Sodium hydroxide is most suitable among the alkali metal or alkaline earth metal compounds. Other compounds are lithium hydroxide, calcium hydroxide, magnesium hydroxide, sodium bicarbonate or a combination thereof.

The cellulose material is impregnated with such compound in the form of an aqueous alkaline solution.

An aqueous alkaline solution is necessary to loose lignin contained in lignocellulose material. The final water content of the lignocellulose material to be treated is preferably controlled to 10 to 80% by weight. When a wet lignocellulose material is used, the water content thereof is taken into consideration in impregnation. When the water content is lower than 10%, the degree of loosing lignin may be insufficient. When the water content exceeds 80%, a good gas-solid contact between ozone and lignocellulose material may not be expected. According to the study by the inventors, it has been found that a preferable range of the water content is about 40 to 60% by weight.

The final content of the alkali metal or alkaline earth metal compound un the impregnated lignocellulose material plays an important role. If the alkali metal or alkaline earth metal compound content is less than 0.001% by weight based on the total weight, the degree of loosing of lignin may be insufficient, which results in a difficult of decomposition of lignin by ozone treatment. When the content of the compound is larger than 10% by weight, no substantial further improvement is attained.

Preferably, the content of the compound is 0.01 to 1% by weight. If the amount of the compound is based on the dry cellulose material, a preferable amount is within a range of 0.1 to 10% by weight. When the mixing ratio of the alkaline aqueous solution to the cellulose material is too large, which results in an increase of the amount of water, the pieces of the chopped cellulose material adhere to one another and the area of contact with ozone is decreased. Furthermore, soluble lignin dissolved in water preferentially reacts with ozone, which results in consumption of ozone. If the mixing ratio is adjusted within the above-mentioned range of from 0.1 to 10, the cellulosic material is in a gas-solid contact with an ozone-containing gas.

In the present invention, it is preferred that the ozone treatment be carried out at a temperature of 0 to 100°C and an ozone concentration of about 0.1 to about 20 g/m^3.

We examined various conditions for the ozone treatment of cellulose materials impregnated with an alkaline aqueous solution by using an experimental apparatus described below. The present invention will now be described with reference to the scheme of the apparatus, the operation and the experimental results.

Brief description of the drawings

Fig. 1 is a diagram illustrating the section of an apparatus used at experiments according to the present invention. Fig. 2 is a graph illustrating the relation between the concentration of an aqueous solution of

NaOH and the enzymatic decomposability. Fig. 3 is a graph illustrating the relation between the concentration of an aqueous solution of NaOH and the amount of ozone reacted. Fig. 4 is a graph illustrating the relation between the mixing ratio of an aqueous solution of NaOH to the enzymatic decomposability.

Detailed description of the present invention

Fig. 1 is a diagram illustrating the section of the apparatus used at the experiments. The apparatus comprises an ozone treatment tank 1, a mixing tank 2, a stirring vane 3, an atomizer 4, a compressor 5, an alkaline aqueous solution store tank 6, a moving bed 7, an ozone generator 8, an ozone blow opening 9, a discharge feeder 10, a starting material 11, air 12 and an exhaust gas 13.

In the present apparatus, a cellulose material is impregnated with an alkaline aqueous solution in the mixing tank 2 and is then contacted with ozone in the ozone treatment tank 1.

The alkaline aqueous solution is sprayed on the cellulose material as the starting material 11 from the atomizer 4 in the vicinity of an inlet of the mixing tank 2. The atomizer 4 sprays the alkaline aqueous solution fed from the alkaline aqueous solution store tank 6 with the air of compressed air from the compressor 5. The cellulose material impregnated with the alkaline aqueous solution by spraying is stirred by the stirring vane 3 in the mixing tank 2 and is then fed to the ozone treatment tank 1 and accumulated therein. Then, the cellulosic material is withdrawn from the lower portion of the ozone treatment tank 1 by the discharge feeder 10. During this period, the cellulose material impregnated with the alkaline aqueous solution is gradually brought down. Ozone-containing air prepared in the ozone generator 8 is blown into the ozone treatment tank 1 from the ozone blow opening 9 located in the lower portion of the ozone treatment tank 1. The cellulose material impregnated with the alkaline aqueous solution is contacted with the ozone-containing air in a counter-current manner, and the cellulose material is reacted with ozone and the ozone-containing gas is consumed in the ozone treatment tank 1 and discharged outside the apparatus.

The present invention will now be described in detail with reference to the following Examples that by no means limit the scope of the invention.

Example 1

Rice straw cut into a length of 5 to 10 mm was used as the cellulosic material, and it was impregnated with an alkaline aqueous solution and subjected to the ozone treatment. The enzymatic decomposability of rice straw cellulose by a cellulase was then examined.

Sodium hydroxide (hereinafter referred to as "NaOH") was used as the alkaline substance, and various aqueous solutions of NaOH differing in concentration in the range of 0.001 to 20% by weight were prepared. The rice straw was mixed with the aqueous solution of NaOH at a weight ratio of 1/1 to impregnate the rice straw with the aqueous solution of NaOH. The final content of NaOH is 0.1 mg to 2 g per 10 g of dry cellulose and the water is 8 to 10 g per 10 g of dry cellulose. Accordingly, the NaOH content is 0.0005 to 10% by weight based on the total weight of the aqueous solution and cellulosic material. The ozone concentration in ozone-containing air to be blown into the ozone treatment tank 1 was kept at a constant level of 12 g/m^3, and the treatment was carried out at room temperature (21±2°C).

The enzymatic decomposability of each of the so-treated rice straws by a commercially available cellulase (derived from *Trichoderma reesei* and supplied by Amano Seiyaku Kabushiki Kaisha) was measured. The enzymatic decomposability was defined as the amount (mg) of glucose formed for 1 hour by one unit of the enzymatic activity of the cellulase (1 U: the amount of the cellulase forming 1 μ-mole of glucose for 1 minute by 1 ml of the enzyme solution by using carboxymethyl cellulose as the substrate). At the measurement, 100 mg (dry weight) of the treated rice straw was mixed with 2 ml of a 1/20 M citric acid buffer solution (having a pH value of 4.8) and 2 ml of the enzyme solution, and the mixture was shaken at 50°C for 1 hour. After completion of the reaction, the enzyme was deactivated and the amount of the reducing sugar formed was measured.

For comparison, the measurement was carried out on a sample which had not been subjected to the ozone treatment.

The obtained results are shown in Fig. 2. Namely, Fig. 2 is a graph illustrating the relation between the concentration of the aqueous solution of NaOH and the enzymatic decomposability. In Fig. 1, curve A shows the results obtained according to the present invention and curve B shows the results obtained when the ozone treatment was not carried out.

As is seen from the graph of Fig. 2, when the concentration of the aqueous solution of NaOH was 0%, that is, water alone was used, and the impregnated rice straw was subjected to the ozone treatment, the enzymatic decomposability was 3.1 mg-glucose/U · hour at highest, and if the concentration of the aqueous solution of NaOH was 0.005% by weight or higher, the enzymatic decomposability was improved. Furthermore, if the concentration of the aqueous solution of NaOH was higher than 5% by weight, even if the impregnated rice straw was not subjected to the ozone treatment, the enzymatic decomposability was improved, but the degree of improvement was much lower than in case of the impregnated rice straw which had been subjected to the ozone treatment.

Example 2

The treatment was carried out in the same manner as described in Example 1, and the amount of ozone reacted per 1 kg (dry weight) of the rice straw was measured.

The amount of reacted ozone was calculated from the difference of the ozone concentration between the inlet and outlet of the ozone treatment tank 1, the feed rate of the ozone-containing air and the contact time.

The obtained results are shown in Fig. 3 which is a graph showing the relation between the concentration of the aqueous solution of NaOH and the amount of reacted ozone. As is seen from Fig. 3, the amount of reacted ozone was abruptly increased when the concentration of the aqueous solution of NaOH exceeded 15% by weight. In the light of the results shown in Fig. 2, it is seen that if the concentration of the aqueous solution of NaOH is higher than 15% by weight or the content of NaOH is larger than about 10% based on the total weight of the aqueous solution and cellulose, the amount of reacted ozone is consumed by the alkaline compound and the enzymatic decomposability is hardly increased. Accordingly, it is considered that this increased amount of reacted ozone is an apparent amount of reacted ozone and the enzymatic decomposability is not substantially improved but ozone is merely decomposed by the alkali.

From the results obtained in Examples 1 and 2, it can be concluded that an effective and economical concentration of the aqueous solution of NaOH is in the range from 0.005 to 15% by weight, especially 0.1 to 1% by weight. This amount corresponds to about 0.001 to 10% of an alkaline substance by weight based on the total weight of the alkaline solution and the cellulosic material. Preferably, the content of alkaline substance should be about 0.01 to 1% by weight.

Example 3

The concentration of the aqueous solution of NaOH was adjusted to 0.1, 0.5 or 1% by weight, and the relation between the mixing weight ratio of the rice straw and the aqueous solution of NaOH and the enzymatic decomposability was examined.

With respect to each of the aqueous solutions of NaOH, the mixing weight ratio was adjusted within the range of from 0.1 to 20 and the ozone treatment was carried out under the same conditions as adopted in Example 1.

The obtained results are shown in Fig. 4, which is a graph showing the relation between the mixing weight ratio of the aqueous solution of NaOH and the rice straw and the enzymatic decomposability, and curves C, D and E shows the results obtained when the concentrations of the aqueous solutions of NaOH were 0.1, 0.5 and 1% by weight, respectively.

From Fig. 4, it is seen that in each case, if the mixing weight ratio was at least 0.1, the enzymatic decomposability was improved and especially good results could be obtained when the mixing weight ratio was in the range of from 1 to 7. It also is seen that if the mixing weight ratio exceeded 7, the enzymatic decomposability was reduced and this reduction was extreme if the mixing weight ratio was 20 or higher.

From the foregoing results, it will readily be understood that the mixing weight ratio of the aqueous solution of NaOH to rice straw should be about 0.1 to about 10, preferably 1 to 7. When the content of the aqueous solution is expressed in terms of water content, it should be within a range of about 10 to 80% by weight, preferably about 40 to 60% by weight.

Example 4

Bagasse, wood dust, newspaper and corn stover were impregnated separately as the cellulosic material with an aqueous solution of NaOH and was then subjected to the ozone treatment in gas-solid contact, and the enzymatic decomposability was examined. The concentrations of the aqueous solution of NaOH was adjusted to 0.1% by weight, and the mixing weight ratio of the aqueous solution of NaOH to the cellulosic material was adjusted to 1. The ozone treatment was carried out under the same conditions as adopted in Example 1. For comparison, the cellulose material was impregnated with water (water/cellulosic material weight ratio=1/1) and was then subjected to the ozone treatment, and the enzymatic decomposability was examined. Furthermore, the ozone decomposability of the sample which was not subjected to the ozone treatment (untreated sample) was examined.

The obtained results are shown in Table 1.

TABLE 1

Cellulose material	Treatment	Enzymatic decomposability (mg-glucose/U · hour)
bagasse	impregnation with NaOH aqueous solution and ozone treatment in gas-solid contact	6.8
"	impregnation with water and ozone treatment in gas-solid contact	3.3
"	untreated	1.2
wood dust	impregnation with NaOH aqueous solution and ozone treatment in gas-solid contact	5.2
"	impregnation with water and ozone treatment in gas-solid contact	2.5
"	untreated	0.5
newspaper	impregnation with NaOH aqueous solution and ozone treatment in gas-solid contact	4.2
"	impregnation with water and ozone treatment in gas-solid contact	2.8
"	untreated	1.6
corn stover	impregnation with NaOH aqueous solution and ozone treatment in gas-solid contact	5.8
"	impregnation with water and ozone treatment in gas-solid contact	3.0
"	untreated	1.0

From the results shown in Table 1, it will readily be understood that excellent effects can be obtained according to the method of the present invention.

Example 5

Sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium bicarbonate, calcium hydroxide and magnesium hydroxide were used as the alkali metal or alkaline earth metal compound, and the effects were examined.

Rice straw was used as the cellulosic material. The concentration of each alkaline aqueous solution was adjusted to 1.0% by weight, and the mixing weight ratio of the alkaline aqueous solution to rice straw was adjusted to 1. The ozone treatment was carried out under the same conditions as adopted in Example 1. The enzymatic decomposability of each treated rice straw was examined in the same manner as described in Example 1. The obtained results are shown in Table 2.

TABLE 2

Alkali metal or alkaline earth metal compound	Enzymatic decomposability (mg-glucose/U · hour)
sodium hydroxide	7.0
potassium hydroxide	6.8
lithium hydroxide	6.0
sodium bicarbonate	4.2
calcium hydroxide	5.5
magnesium hydroxide	3.8

From the results shown in Table 2, it will readily be understood that even when alkali metal or alkaline earth metal compounds in place of sodium hydroxide are used, the enzymatic decomposability can be improved since the enzymatic decomposability can be improved since the enzymatic decomposabilities of water-impregnated ozone-treated and untreated rice straw are about 3.0 mg-glucose/U · hour and about 0.9 mg-glucose/U · hour, respectively.

Example 6

The utilizability of rice straw impregnated with an aqueous solution of NaOH and treated with ozone, by a cellulose decomposing fungus was examined to find whether or not cellulose of such rice straw could be utilized as a nutritive source.

The concentration of the aqueous solution of NaOH was adjusted to 0.1% by weight, and the mixing weight ratio of the aqueous solution of NaOH to rice straw was adjusted to 1. As the cellulose decomposing fungus, there were used *Trichoderma reesei* American Type Culture Collection (ATCC) No. 13631 and *Cellulomonas flavigena* (ATCC No. 484).

A culture medium used for culturing comprised 6.0 g/l of sodium chloride, 1.0 g/l ammonium sulfate, 0.5 g/l of monopotassium phosphate, 0.5 g/l of dipotassium phosphate, 0.2 g/l of magnesium sulfate, 0.3 g/l of calcium chloride and 1.0 g/l of yeast extract. The concentration of rice straw was adjusted to 10 g/l. Culturing was conducted at 30°C for 10 days.

As the index of the utilizability by the cellulose decomposing fungus, the amount of proteins formed by the cellulose decomposing fungus was determined by subtracting the amount of protein contained in the rice straw from the protein contained in the culture medium. The obtained results are shown in Table 3. For comparison, the experiment was carried out without performing the ozone treatment (untreated). The obtained results are also shown in Table 3.

TABLE 3

Cellulose decomposing fungus	Treatment	Amount of formed protein (g-protein per g-dry rice straw)
Trichoderma reesei	impregnation with NaOH aqueous solution and ozone treatment in gas-solid contact	0.075
"	untreated	0.001
Cellulomonas flavigena	impregnation with NaOH aqueous solution and ozone treatment in gas-solid contact	0.097
"	untreated	0.015

From the results shown in Table 3, it will readily be understood that when impregnation with an aqueous solution of NaOH and ozone treatment are carried out according to the present invention, the amount of propagation of a cellulose decomposing fungus is increased and utilizability of rice straw by the cellulose decomposing fungus can be increased.

As will be apparent from the foregoing description, if a cellulosic material is impregnated with an alkaline aqueous solution of an alkali metal or alkaline earth metal compound and is then contacted with

ozone according to the present invention, the biological decomposability characteristics of the cellulosic material, that is, the enzymatic decomposability by a cellulase and the utilizability by a cellulose decomposing fungus, can be improved. Especially good results can be obtained when a cellulosic material is impregnated with sodium hydroxide at a concentration of 0.001 to 10% by weight and at the water content in the cellulosic material of 10 to 80% and the cellulosic material is then subjected to the ozone treatment, keeping gas-solid contact between the cellulosic material and ozone. The method of the present invention is very simple. And, since the amount used of water is small, a problem of the waste water treatment does not occur. Furthermore, the pretreatment method of the present invention can effectively be applied to not only manufacture of glucose and microorganism protein from cellulosic materials but also conversion of cellulosic materials to valuable substances by using microorganisms capable of methane fermentation or organic acid fermentation.

The present process consumes only a very small amount of energy, because the process uses a small amount of water which dissolves low molecular weight compounds that decomposes ozone. Accordingly, the required energy for generating ozone is smaller than the process in which cellulose material is suspended in water. Further, in the process of the present invention the lignin, which is loosed by the impregnated alkaline solution, is effectively decomposed, because ozone can attack the lignin in gas-solid contact.

Claims

1. A method for the pretreatment of lignocellulose materials for biologically or enzymatically decomposing cellulose materials, in which a cellulose material is treated with an alkaline aqueous solution of an alkali metal or alkaline earth metal compound and afterwards with ozone, characterized in that after the treatment with the alkaline solution the cellulose material is immediately treated with ozone in the state of gas-solid contact.

2. A method for the pretreatment of cellulose materials according to claim 1, wherein the water content of the cellulose material is 10 to 80% by weight.

3. A method for the pretreatment according to claim 1 or 2, wherein the content of alkali metal or alklaine earth metal compound is 0.001 to 10% by weight based on the total weight of the alkaline aqueous solution and the cellulose material.

4. A method for the pretreatment according to any of claims 1 to 3, wherein the water content of the cellulose material is about 40 to 60% by weight.

5. A method for the pretreatment according to any of claims 1 to 4, wherein the content of an alkali metal or alkaline earth metal compound is 0.01 to 1% by weight based on the total weight of the alkaline solution and the cellulose material.

6. A method for the pretreatment according to any of claims 1 to 3, characterized in that the cellulose material is chopped and impregnated with the alkaline aqueous solution in such a manner that interstices remain in the chopped cellulose material.

7. A method for the pretreatment according to any of the claims 1 to 6, wherein the alkali or alkaline earth metal compound is selected from the group consisting of sodium hydroxide, lithium hydroxide, calcium hydroxide, magnesium hydroxide, sodium bicarbonate and mixtures thereof.

8. A method for the pretreatment according to any of the claims 1 to 7, wherein the cellulose material is contacted with ozone at a temperature of 0° to 100°C and at an ozone concentration of about 0.1 to about 20 g/m^3.

Patentansprüche

1. Verfahren zur Vorbehandling von Lignozellulosematerialien für die biologische der enzymatische Zersetzung von Zellulosematerialien, bei dem ein Zellulosematerial mit einer wässrigalkalischen Lösung einer Alkalimetall- oder Erdalkalimetallverbindung und danach mit Ozon behandelt wird, dadurch gekennzeichnet, daß das Zellulosematerial unmittelbar nach der Behandlung mit der alkalischen Lösung im Zustand eines Gas-Feststoff-Kontakts mit Ozon behandelt wird.

2. Verfahren zur Vorbehandlung von Zellulosematerialien nach Anspruch 1, bei dem der Wassergehalt des Zellulosematerials 10 bis 80 Gewichtsprozent beträgt.

3. Verfahren zur Vorbehandlung nach Anspruch 1 oder 2, bei dem der Gehalt an Alkalimetall- oder Erdalkalimetallverbindung 0,001 bis 10 Gewichtsprozent, bezogen auf das Gesamtgewicht aus wässrig-alkalischer Lösung und Zellulosematerial, beträgt.

4. Verfahren zur Vorbehandlung nach einem der Ansprüche 1 bis 3, bei dem der Wassergehalt des Zellulosematerials etwa 40 bis 60 Gewichtsprozent beträgt.

5. Verfahren zur Vorbehandlung nach einem der Ansprüche 1 bis 4, bei dem der Gehalt an Alkalimetal- oder Erdakalimetallverbindung 0,01 bis 1 Gewichtsprozent, bezogen auf das Gesamtgewicht von alkalischer Lösung und Zellulosematerial, beträgt.

6. Verfahren zur Vorbehandlung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Zellulosematerial zerschnitten und in der Weise mit der wässrig-alkalischen Lösung getränkt wird, daß in dem geschnittenen Zellulosematerial Zwischenräume verbleiben.

7. Verfahren zur Vorbehandlung nach einem der Ansprüche 1 bis 6, bei dem die Alkalimetall- oder Erdakalimetallverbindung aus der Natriumhydroxid, Lithiumhydroxid, Kalziumhydroxid, Magnesiumhydroxid, Natriumbicarbonat und Gemische davon umfassenden Gruppe ausgewählt wird.

8. Verfahren zur Vorbehandlung nach einem der Ansprüche 1 bis 7, bei dem das Zellulosematerial mit Ozon bei einer Temperatur von 0 bis 100°C und bei einer Ozonkonzentration von etwa 0,1 bis etwa 20 g/m³ in Berührung gebracht wird.

Revendications

1. Procédé de pré-traitement de matières lignocellulosiques pour décomposer biologiquement ou enzymatiquement des matières cellulosiques, dans lequel une matière cellulosique est traitée par une solution aqueuse alcaline d'un composé métal alcalin ou alcalinoterreux, puis par de l'ozone, caractérisé par le fait qu'après le traitement par la solution alcaline, la matière cellulosique est immédiatement traitée par l'ozone par contact gaz-solide.

2. Procédé de pré-traitement de matières cellulosiques selon la revendication 1, caractérisé par le fait que la teneur en eau de la matière cellulosique est de 10 à 80% en poids.

3. Procédé pour le pré-traitement selon la revendication 1 ou 2, caractérisé par le fait que la teneur en composé métal alcalin ou alcalino-terreux est de 0,001 à 10% en poids par rapport au poids total de la solution aqueuse alcaline et de la matière cellulosique.

4. Procédé pour le pré-traitement selon l'une quelconque des revendications 1 à 3, caractérisé par le fait que la teneur en eau de la matière cellulosique est d'environ 40 à 60% en poids.

5. Procédé pour le pré-traitement selon l'une quelconque des revendications 1 à 4, caractérisé par le fait que la teneur en composé métal alcalin ou alcalino-terreux est de 0,01 à 1% en poids par rapport au poids total de la solution alcaline et de la matière cellulosique.

6. Procédé de pré-traitement selon l'une quelconque des revendications 1 à 3, caractérisé par le fait que la matière cellulosique est coupée en morceaux et imprégnée avec la solution aqueuse alcaline de telle manière que des interstices subsistent dans la matière cellulosique coupée en morceaux.

7. Procédé de pré-traitement selon l'une quelconque des revendications 1 à 6, caractérisé par le fait que le composé métal alcalin ou alcalino-terreux est choisi dans le groupe constitué par l'hydroxyde de sodium, l'hydroxyde de lithium, l'hydroxyde de calcium, l'hydroxyde de magnésium, le bicarbonate de sodium et des mélanges de ceux-ci.

8. Procédé de pré-traitement selon l'une quelconque des revendications 1 à 7, caractérisé par le fait que la matière cellulosique est mise en contact avec l'ozone à une température de 0 à 100°C et à une concentration d'ozone d'environ 0,1 à environ 20 g/m³.

FIG. 1

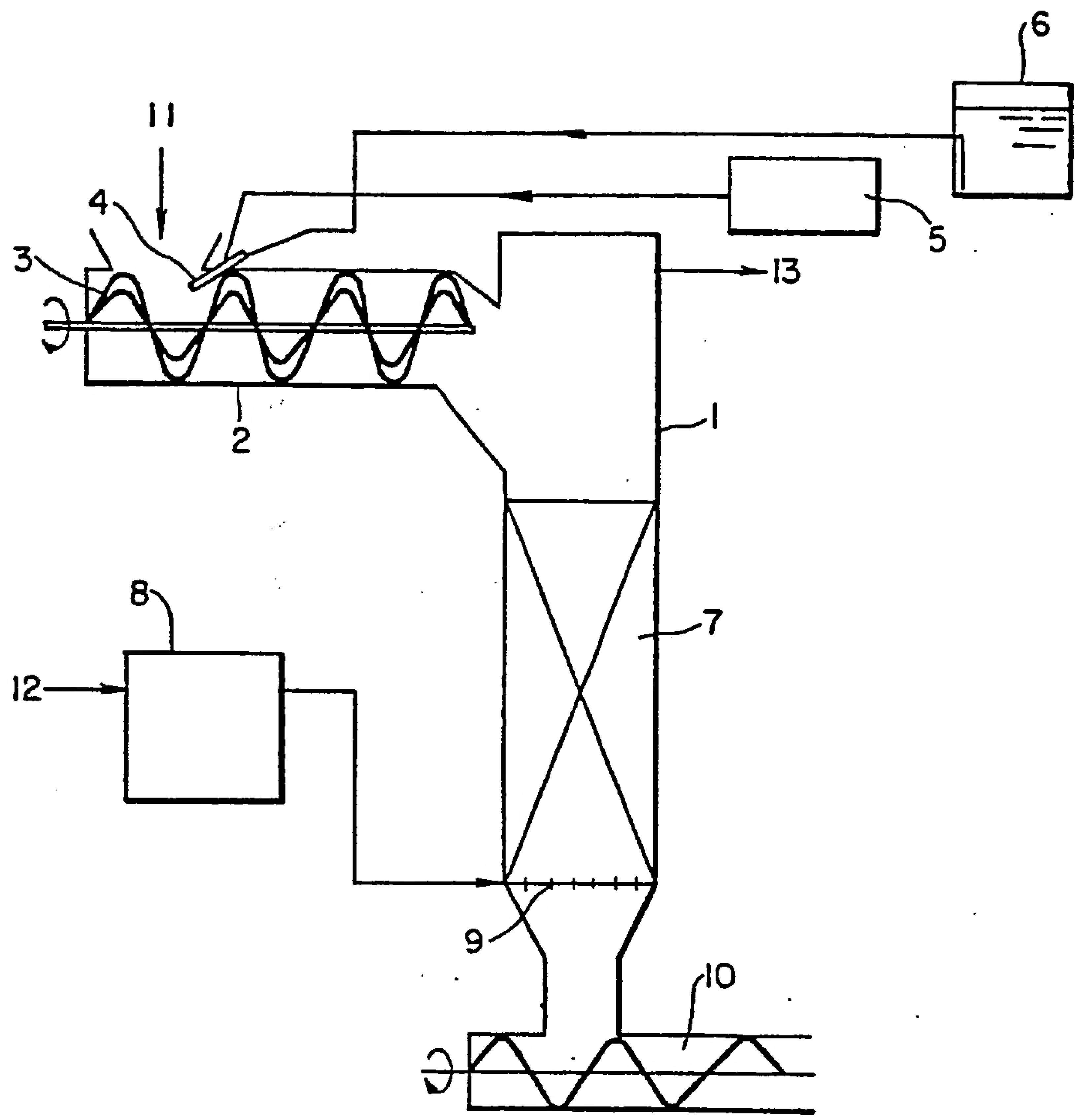


FIG. 2

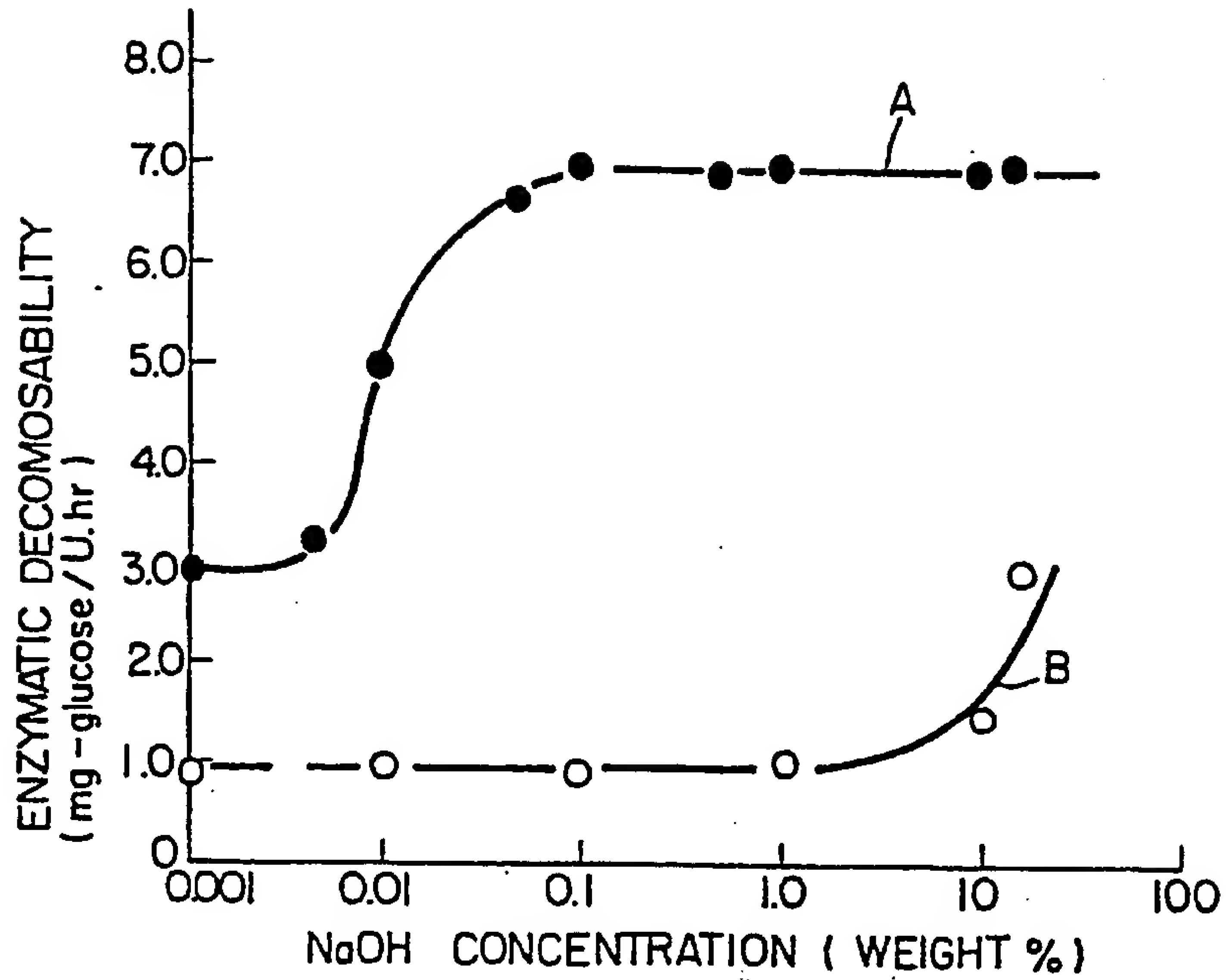

8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
A
B
ENZYMATIC DECOMOSABILITY
(mg -glucose / U.hr)
0.001
0.01
0.1
1.0
10
100
NaOH CONCENTRATION (WEIGHT %)

FIG. 3

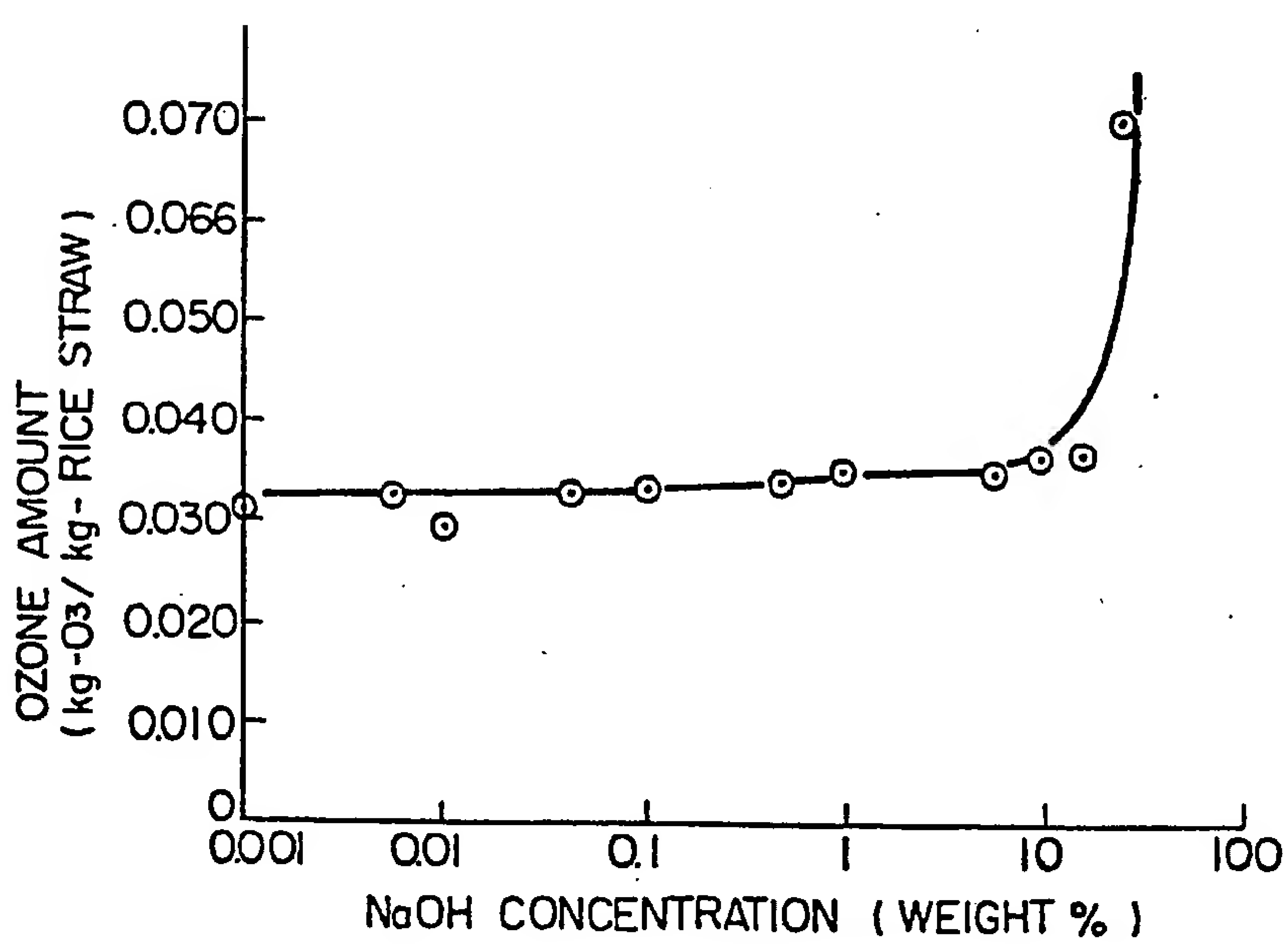
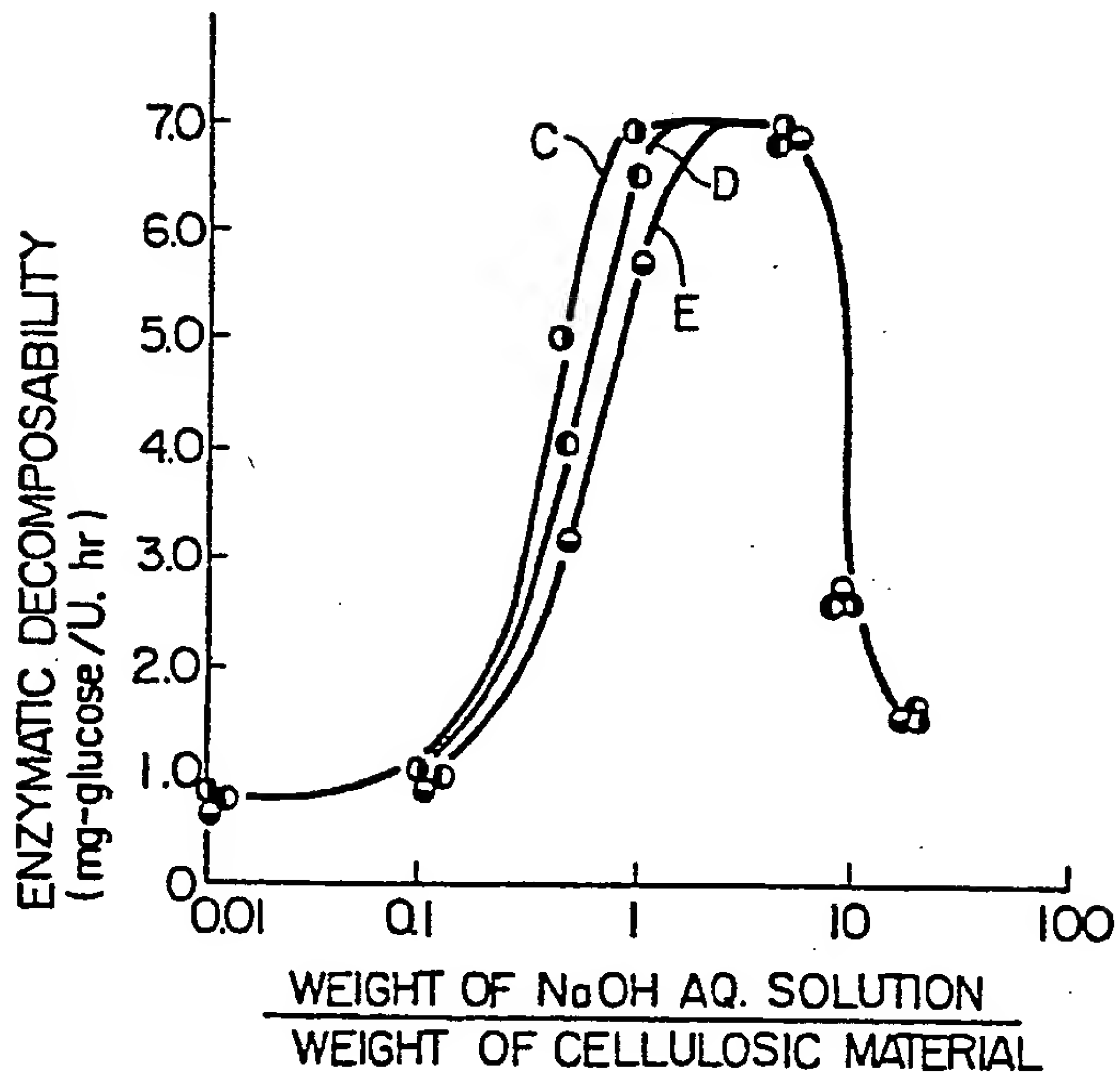

0.070
0.066
0.050
0.040
0.030
0.020
0.010
0
OZONE AMOUNT
(kg-O3/ kg- RICE STRAW)
0.001
0.01
0.1
1
10
100
NaOH CONCENTRATION (WEIGHT %)

FIG. 4


ENZYMATIC DECOMPOSABILITY
(mg-glucose/U. hr)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.01
0.1
1
10
100
C
D
E
WEIGHT OF NaOH AQ. SOLUTION
WEIGHT OF CELLULOSIC MATERIAL